

FEDERAL REPUBLIC OF GERMANY

Cl. 12i 39

GERMAN PATENT OFFICE

INTERNATIONAL CL. C 01 b

PATENT APPLICATION LAID OPEN 1 142 159

K 41302 IV a/12i

Application date: 27 July 1960
Publication of the
application and
issuing of the
application laid open: 10 JANUARY 1963

Method and Device for Production of Lower Titanium Chlorides

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The invention concerns a method for continuous production of lower titanium chlorides from titanium tetrachloride making use of hydrogen as reducing agent, as well as a device to carry out the method of the invention.

According to the methods which have become known thus far making use of hydrogen as reducing agent, one can obtain the pure subhalides, but these methods all operate discontinuously, and as a rule one can only produce quantities of several grams or at best a kilogram. In some of these methods, for example, a mixture of $TiCl_4$ and H_2 is taken through a red-hot pipe and then quenched quickly on an indirectly cooled surface. If one wishes to adopt this method to produce rather large quantities, a whole series of difficulties emerge.

First, all vessel materials are corroded by the hydrogen chloride gas arising during the reduction in the technical implementation at $600^\circ C$ or higher. Furthermore, the cooled surface used for the quenching is coated with a layer of reaction product, which acts as a thermal insulation and therefore impairs the quenching of additional reaction gas.

In other methods, a mixture of $TiCl_4$ and H_2 is taken through an electrical discharge device and then cooled down. Similar difficulties occur here in regard to the choice of vessel material and the quenching of reaction material. Furthermore, it is notoriously difficult to increase an electrical discharge at will to the desired extent and develop a large apparatus.

A mixture of H_2 and $TiCl_4$ has already been reduced in an arc. However, as is easy to understand, major difficulties occur in regard to the material of the electrode jacket and the walls of the vessel.

All these drawbacks of the illustrated methods are overcome when one mixes hydrogen previously heated to high temperatures with $TiCl_4$ in a mixing device such as a nozzle maintained at relatively low temperature, the latter being reduced by the hydrogen present, and the resulting reaction mixture is quenched on a moving cooled surface, which is continuously cleaned by a stationary doctoring device. In this way, one obtains good yields of a mixture of lower halides of titanium with very good purity. The

temperatures at which the mixing nozzle is maintained range between the boiling point of $TiCl_4$ and below around $500^\circ C$, preferably at $200^\circ C$.

The hydrogen must be preheated to temperatures of over $1000^\circ C$, preferably over $2500^\circ C$, in order to achieve an economically feasible yield. The heating of the hydrogen is advisedly done by electrical means, e.g., in an arc, since an indirect heating of hydrogen to temperatures of $1000^\circ C$ or more in a heat exchanger causes considerable difficulties due to the hydrogen-permeability of the walls of the vessel. If one heats the hydrogen in an electric arc, the temperature generated is usually so high that at least a portion of the hydrogen is present in the form of atoms. One can use with special success an arc arrangement such as that described in the documents of German utility model 1 781 880.

In order to achieve a good yield, it is necessary to mix the reaction participants as quickly as possible in the gas phase. This can be accomplished by letting the heated hydrogen flow through a channel with circular cross section and taking the gaseous $TiCl_4$ which has been heated above its boiling point through an annular slot situated in this channel, approximately perpendicular to the channel. It is advantageous to evaporate the $TiCl_4$ under a certain pressure, so that the $TiCl_4$ vapor is taken to the preheated hydrogen at a relatively high speed. In order to increase the exit velocity of the $TiCl_4$ vapor, one can also mix in some hydrogen gas. However, it is also possible to introduce the $TiCl_4$ or the $TiCl_4:H_2$ mixture tangentially into a channel of circular cross section through which hot H_2 is flowing. In any case, it is important to mix together the two reaction partners as quickly as possible.

After this, the reaction gases are taken to a moving cooled surface and thereby quenched. This moving cooled surface is cleaned of reaction product separating out as a loose coating by means of a doctoring device, such as a stationary blade or a brush, so that the arriving reaction gases always encounter a clean surface, which produces a very intense quenching - especially also due to the high thermal conductivity of the hydrogen which is used in excess. The reaction products are captured in a container under inert gas.

In the methods known thus far, the quenching is generally accomplished by spraying in cold liquids. When quenching very hot gases in this way, it is necessary to use a thermally stable liquid, and also one that does not react with the reaction products. In the method of the present invention, however, it is not possible to find such a liquid, since on the one hand stable liquids like H_2O , in particular, react with the reaction product, and on the other hand the liquids which are indifferent to the reaction product, such as organic liquids (benzene, toluene, decaline), are decomposed by the hot reaction gases with partial deposition of carbon, so that one cannot obtain any pure reaction product in this way. Furthermore, it is very difficult to separate substances as sensitive as the lower titanium chlorides from such a quenching liquid.

Moreover, an apparatus functioning with a circulating quenching agent is more complicated than the apparatus used to carry out the present method, in which all parts of such a quenching circuit (pump, heat exchanger, supply tank) are eliminated. Furthermore, the caloric content of the gases being quenched is lost in the quenching methods, while in the method of the invention a recovery of energy is possible under certain circumstances, e.g., in the form of hot water or even steam.

The moving cooled surface must be located inside a housing closed off from the outer atmosphere, since the desired reaction products would react even with traces of oxygen or water vapor. Also, the starting substances, H_2 and $TiCl_4$, must be free of O_2 , N_2 , and other impurities if one wishes to obtain a pure reaction product. If the temperature of the cooled surface is kept too low, the separated reaction products will absorb unreacted $TiCl_4$. Thus, it is advantageous to keep the temperature high enough so that such an absorption is largely prevented. For example, the cooling agent such as water with which the moving surface is cooled during the production of lower titanium halides can be kept cooled to temperatures of 50 to $300^\circ C$, preferably 50 to $100^\circ C$, in order to obtain an end product with content of $TiCl_4$ under around 2% .

Moreover, it is necessary to use hydrogen in excess from the stoichiometric quantity resulting from the reaction equation. In experiments, a 1.2 to twenty-fold, preferably a ten to fifteen-fold excess of H_2 has proven to be advantageous.

If one selects the molar ratio of $H_2:TiCl_4$ smaller than around 5, one generally gets almost exclusively $TiCl_3$, besides unreacted $TiCl_4$. If one increases this ratio, increasing quantities of $TiCl_2$ occur as reaction product in the resulting $TiCl_3$.

The space and time yield is greater than 0.15 kg/l-h , and the reaction product occurs in the form of a finely divided pyrophoric powder, which oxidizes in air by glowing and giving off a white cloud.

The reaction products stripped off are captured under inert gas in a container located beneath the housing of the cooling roller. The escaping gases contain, besides unreacted $TiCl_4$, also reaction products in the form of dust, and a considerable amount of lower titanium halides are still contained in the outgoing

gas. They are removed from the outgoing gas by a dry gas cleaning. Once again, it is necessary to maintain the walls of the dust removal apparatus at such temperatures as prevent a condensation of unreacted $TiCl_4$. These temperatures are dependent on the partial $TiCl_4$ pressure prevailing in the apparatus and should be around 5 to 100°C above the dew point of the $TiCl_4$ corresponding to the particular operating conditions. The dust separation can occur, for example, with cyclones, baffles, or settling tanks.

The unreacted $TiCl_4$ is separated from the dust-free exhaust gases by cool down in familiar fashion and can then be returned to the process. The cool down can occur in two stages, for example, in a first liquid condensation stage operating above the melting point of $TiCl_4$ (-23°C) and in a second solid condensation stage operating below the melting point. The hydrogen used in excess will afterwards contain only hydrogen chloride, which can be removed from it by absorption, for example, using an appropriate device, so that the hydrogen can then be dried and used again for reduction.

The substances produced by the method of the invention are very pure. Thus, e.g., one can get products consisting of more than 99.8% titanium and chlorine from the reduction of $TiCl_4$. This is especially important if one wishes to run the process as a preliminary stage in the obtaining of titanium metal.

The drawings show schematically devices for carrying out the method of the invention, namely:

Figure 1, the side view of a device in which the moving and cooled surface has the shape of a cylinder, in cross section along line I-I of figure,

Figure 2, the device in section along line II-II of figure 1,

Figure 3, a device in which the moving and cooled surface has the shape of a cone, in lengthwise section.

Figures 1 and 2 show a technical embodiment of the device.

Hydrogen introduced into the burner at 13 is heated hot as it passes through the arc burning between cathode 4 and anode 5. In the mixing nozzle 6, gaseous titanium tetrachloride, introduced via the line 14, is added to the heated hydrogen, partially split up into atoms. Burner and mixing nozzle 6 lie in a recess of the housing cover 3. The reaction products, as well as unreacted starting substances, impinge on the moving cooled roller 1. A cooling agent of around 50 to 300°C, such as water or oil, is sprayed from the inside through a perforated pipe 7, situated in the axle of the roller, against the segment of the roller 1 that is closest to the burner. The bottom half of the roller 1 is filled with the cooling agent arriving from the upper part. The excess leaves the roller 1 through an open cylinder at 9. The cooling roller 1 is surrounded by a housing 2, which is enclosed in a cooling jacket 10. The solid reaction products clinging to the surface of the roller 1 and to the inner wall of the vessel 2 are removed by a blade 17 secured to the housing and by a pivoting blade 16. The movable blade 16 can be activated by a crank 15 or some other mechanical drive unit in its place. The reaction products drop into a catching vessel 19. The exhaust gases leave the apparatus through the line 18, to be taken through additional separation apparatus, such as cyclones or baffles.

A further embodiment of the method can be carried out with the apparatus shown by figure 3. Here, the quenching and separation of the reaction products occur on a rotating cone, whose tip faces the spray nozzle. The other parts of the apparatus are analogous to those of figure 1 and require no special explanation.

Other embodiments of the present method also involve letting the heated hydrogen flow through a channel with circular cross section and supplying the $TiCl_4$ or the mixture of $TiCl_4$: H_2 to the hydrogen either through an annular slot 21 emerging into this channel 20, roughly perpendicular to its direction of flow, or tangentially to this channel 20.

In order to increase the economy of the method, the titanium tetrachloride and hydrogen exhaust gases which have been cleaned of powderlike reaction products and HCl in familiar fashion can be recycled into the reaction process after they have been separated from each other in likewise familiar fashion.

Example 1

4750 parts by weight of $TiCl_4$, at an average flow velocity of the liquid $TiCl_4$ in the evaporator of 9.5 kg/h, were caused to react with 2.25 Nm³ of hydrogen heated in an arc in the gaseous state according to the reaction equation.



This corresponds to an eight-fold excess of hydrogen per equation (1). The flow rate of the hydrogen was 4.5 Nm³/h. The temperature of the mixing nozzle was maintained at 150°C by air cooling. The energy in the arc for heating of the hydrogen was 22 kWh (135 Amp., 325 Volts in 30 minutes). One got 2320 parts by weight of pure TiCl₃.

Yield: 60% (in terms of the TiCl₄ used).

Example 2

3340 parts by weight of TiCl₄ were evaporated (flow rate of the fluid substance in the evaporator 6.68 kg/h) and added to 2.25 Nm³ hydrogen heated in an arc. This corresponds to an 11.4-fold excess per equation (1). The flow rate of the hydrogen was 4.5 Nm³/h. The amount of energy supplied to the arc for the heating of the hydrogen was 25 kWh (145 Amp., 345 Volts in 30 minutes). One got a mixture of 1810 parts by weight of lower titanium halides (6% TiCl₂ + 94% TiCl₃).

Yield: 67.5%.

Example 3

5900 parts by weight of TiCl₄ moved at a flow rate of 5.9 kg/h into the evaporator and were reacted with 4.5 Nm³ of hydrogen in the gas state. The flow rate of the hydrogen was 4.5 Nm³/h. The quantity used corresponds to a 13-fold excess per equation (1). The amount of energy supplied to the arc for the heating of the hydrogen was 48 kWh (150 Amp., 320 Volts in 60 minutes). One got a mixture of 3020 parts by weight of lower titanium halides (7% TiCl₂ + 93% TiCl₃).

Yield: 64.5%.

CLAIMS:

1. Method for continuous production of lower titanium chlorides by reduction of titanium tetrachloride with an excess of hydrogen in the gas phase and quenching of the reaction products on a cooled surface, characterized in that the hydrogen previously heated to temperatures of over 1000°C is mixed quickly and intimately with the titanium tetrachloride and allowed to react with it inside a mixing zone maintained at temperatures between the boiling point of titanium tetrachloride and roughly 500°C, preferably 200°C, whereupon the reaction products impinge on the surface cooled to 50 to 300°C, preferably 50 to 100°C, which is moving in familiar manner and is constantly cleaned of the reaction products being precipitated on it, and the latter are then captured under inert gas.

2. Method per Claim 1, characterized in that the heating of the hydrogen is done by means of an arc arrangement.

3. Method per Claim 1 and 2, characterized in that hydrogen is additionally added to the titanium tetrachloride before entering the mixing device.

4. Device to carry out the method of Claim 1 to 3, consisting of a closed housing provided with exhaust gas line and removal arrangement, in which a hollow body which can be cooled and which is provided with doctoring devices can turn about its axle, characterized in that an arc arrangement with an attached mixing device (6), preferably a nozzle, for mixing the TiCl₄ with the stream of hydrogen heated hot in the arc, is located across a recess of the cover (3) in the housing (2), and the hollow body has inside it a supply pipe (7) for cooling agent, provided with holes or nozzles, and also a drainage pipe (9), wherein the doctoring device consists of a blade (17) firmly connected to the housing (2) in familiar fashion and a blade (16) which can be turned by a crank (15).

5. Device per Claim 4, characterized in that a channel (20) is provided for the heated hydrogen, coordinated with an annular slot (21) for supplying the TiCl₄.

6. Device per Claim 4, characterized in that the supply of the TiCl₄ emerges tangentially into the channel (20).

7. Device per Claim 4 to 6, characterized in that the cooling surface (1) has the shape of a cone, whose tip faces the spray nozzle (figure 3).

Publications taken into consideration:

German Patent No. 886 446;

German applications laid open No. 1 008 266, 1 072 975;

US patent No. 859 750

"Berichte der Deutschen Chemischen Gesellschaft", Vol. 42, 1909, p. 3200 to 3218.

[plus three pages of drawings]

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PATENT SPECIFICATION

(11) 223055

**USSR
State Committee
on Inventions
and Discoveries**

(61) Supplemental to application ...

(22) Filed 07.07.65 (21) 1021782/23-26
with addition of application No.

(51) Int. Cl.³:
B 01 J 19/00

(23) Priority -

Published 06.15.82 Bulletin No. 22

(53) UDC 533.92:66
.023 (088.8)

Publication date of specification

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(54) A PLASMA-CHEMICAL REACTOR

The invention pertains to plasma apparatus designed to carry out chemical and physical transformations of substances under conditions of low-temperature plasma.

There is a known plasma apparatus with electric arc rotating between coaxial cooled electrodes in the magnetic field of a solenoid. The substances being processed are fed through the rotating arc.

In the existing apparatus, the high-temperature heating zone formed by the rotating arc has a small extent and a sharply defined nonuniformity of the temperature field in the direction perpendicular to the arc. Therefore, the residence time of the substances being processed in the high-temperature volume and the associated depth of transformation of the starting materials, especially when in powderlike form, proves to be inadequate. Furthermore, under conditions of a corrosive environment, the electrodes need intensive cooling in order to prevent them from corroding. This makes it necessary to implement an electric discharge at elevated voltage or to use expendable electrodes. Under conditions of a high-voltage discharge, it is not possible to feed materials producing a rather large conductivity to the processing zone, since this will result in excessive current increase, which is dangerous both to the electrodes and to the electric current source. The use of expendable electrodes makes it possible to implement a low-voltage discharge in the vapor of the electrode material, but it has a very specific nature of application.

In order to create a three-dimensional plasma in the proposed plasma device, the cathode is a plasmatron, while the anode has the shape of a Laval nozzle.

The drawing shows a cross section through the described plasma apparatus.

It consists of a cathode 1, anode 2, solenoid magnet 3, quenching chamber 4, inlets 5 for starting products, a housing 6, and an outlet 7 for the target products.

During operation of the apparatus, the plasma of a low-voltage discharge fills a considerable volume and has geometrical dimensions dictated by the relation $H > 0.5D$, $D > d$, where H and D are respectively the height and diameter (equivalent diameter) occupied by the plasma, and d is the diameter of the plasmatron nozzle.

The plasma volume may have a cylindrical, conical, or any other configuration of surface bounded by the rotation about the axis of the apparatus of a line or curve (for example, a curve corresponding to the profile of a Laval nozzle).

The dimensions H , D and d are found from conditions basically dependent upon the capacity of the plasma apparatus, the nature of the plasma-forming gas, and the properties of the materials being processed.

The low-voltage three-dimensional discharge in the plasma apparatus arises as a result of the fact that the space between the cold electrodes 1 and 2 is filled with conducting gas from the plasmatron.

When the electric field strengths in the column of arc of the plasmatron and in the positive space of the three-dimensional discharge between the cathode and the anode become equal, current will cease to flow to the anode section of the plasmatron and electrons will emerge into the space between the electrodes.

In the volume under the influence of the intersecting electric and magnetic fields, electrons will begin to move in the azimuth and radial directions, and since the relaxation time of the electrons in the volume is much less than the time to move to the anode, the electrons will ionize the gas, creating conditions for conductivity between the electrodes.

When the materials being processed are present in the volume, the flow of electrons will partly surrender its energy directly to carry out the process.

When the electric field strength in the positive space of the three-dimensional discharge is substantially larger than the strength in the column of arc of the plasmatron, the cold cathode will begin to imitate the electrons coming from the anode section of the plasmatron. Such a discharge resembles a discharge between cold electrodes, the only difference being that the discharge under such circumstances is low-voltage.

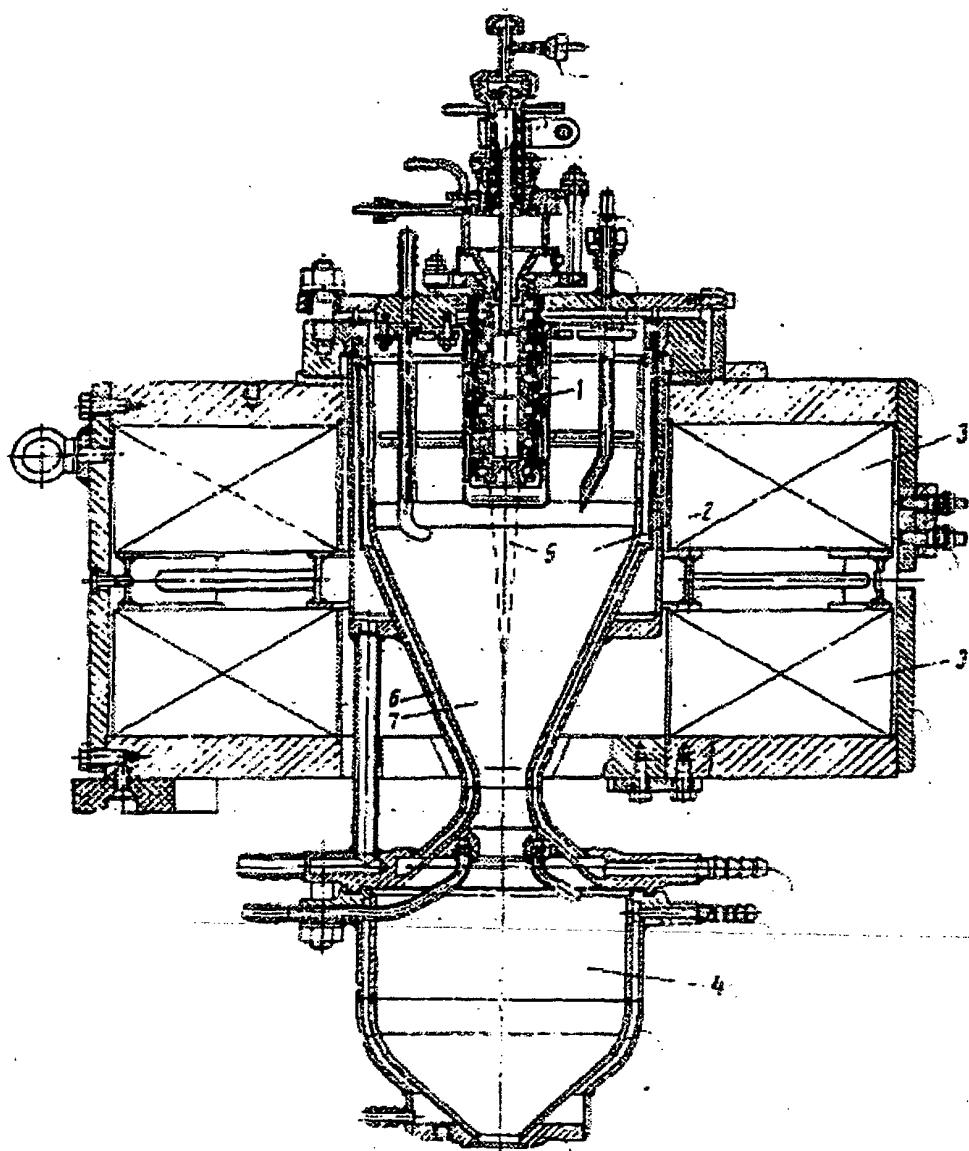
A peculiarity of the movement of the particles under the influence of the intersecting magnetic and electric fields with axial symmetry is the dependency of the speed of movement of the plasma particles on the radius of the orbit of rotation. Such a dependency fosters a more chaotic rotational motion due to turbulent mixing of the plasma layers traveling at different speed.

The substances being processed, fed to the plasma via inlets 5, are entrained by the plasma, atomized and ionized, participating in the mechanism of formation of the plasma and changing its electrical conductivity. The physico-chemical transformations make use of not only the thermal energy of the plasma gas, but also the energy of the elementary particles (electrons, ions). As a result, the efficiency of processing of the substances increases, thermal losses in the electrodes decrease, and the energy efficiency of the apparatus is improved.

PATENT CLAIMS

1. A plasma chemical reactor for carrying out chemical reactions, including a housing, a plasmatron, a cathode, an anode, a solenoid, a quenching chamber, an inlet and outlet for products, characterized in that, to create a three-dimensional plasma, the cathode is a plasmatron.

2. Reactor per Claim 1, characterized in that the anode has the shape of a Laval nozzle.



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